Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

B_{eq} is the mean of the principal axes of the thermal ellipsoids.

	x	y	z	B_{eq}
Cu	0.54953 (7)	0.37260	0.11812 (3)	3.028 (24)
S	0.8669 (3)	0.41871 (16)	−0.11865 (10)	5.81 (8)
O(1)	0.7430 (7)	0.5309 (4)	0.2031 (3)	4.67 (19)
O(2)	0.8382 (5)	0.3486 (3)	0.22944 (20)	4.28 (17)
N(1)	0.5925 (6)	0.5080 (4)	0.16713 (24)	3.54 (17)
N(2)	0.3109 (6)	0.4444 (4)	0.10058 (23)	3.42 (17)
N(3)	0.5157 (5)	0.2181 (4)	0.08695 (21)	3.28 (17)
N(4)	0.7326 (5)	0.2989 (4)	0.18083 (22)	2.95 (15)
N(5)	0.6925 (6)	0.4036 (5)	0.01715 (25)	4.69 (23)
C(1)	0.4981 (10)	0.6918 (5)	0.1847 (4)	5.1 (3)
C(2)	0.4736 (8)	0.5811 (4)	0.1575 (3)	3.68 (22)
C(3)	0.3128 (8)	0.5422 (5)	0.1208 (3)	3.89 (23)
C(4)	0.1583 (10)	0.6158 (6)	0.1099 (4)	5.7 (3)
C(5)	0.1453 (9)	0.4019 (6)	0.0712 (4)	5.4 (3)
C(6)	0.1403 (8)	0.2854 (6)	0.0715 (5)	5.4 (3)
C(7)*	0.2754 (15)	0.2579 (9)	−0.0005 (6)	3.0 (4)
C(7′)*	0.2202 (21)	0.2009 (18)	0.0324 (12)	8.2 (11)
C(8)	0.4020 (9)	0.1834 (7)	0.0244 (3)	5.6 (3)
C(9)	0.6233 (6)	0.1533 (4)	0.1191 (3)	3.10 (19)
C(10)	0.6347 (9)	0.0373 (5)	0.1024 (4)	5.2 (3)
C(11)	0.8598 (8)	0.1320 (5)	0.2242 (3)	4.29 (24)
C(12)	0.7410 (7)	0.1982 (4)	0.1767 (3)	2.82 (19)
C(13)	0.7645 (7)	0.4094 (5)	−0.0385 (3)	3.61 (20)

* Occupancy factor assumed to be 0.5.

Table 2. *Selected distances* (Å) *and angles* (°)

Cu—N(1)	1.954 (5)	N(4)—C(12)	1.279 (7)
Cu—N(2)	2.039 (4)	N(5)—C(13)	1.141 (7)
Cu—N(4)	2.011 (4)	C(1)—C(2)	1.496 (9)
Cu—N(3)	2.049 (5)	C(2)—C(3)	1.464 (9)
Cu—N(5)	2.147 (4)	C(3)—C(4)	1.503 (9)
S—C(13)	1.639 (6)	C(5)—C(6)	1.474 (11)
O(1)—N(1)	1.338 (6)	C(6)—C(7)	1.684 (13)
O(2)—N(4)	1.339 (5)	C(7)—C(8)	1.413 (13)
N(1)—C(2)	1.298 (7)	C(6)—C(7′)	1.415 (20)
N(2)—C(3)	1.289 (8)	C(7′)—C(8)	1.394 (18)
N(2)—C(5)	1.457 (8)	C(9)—C(10)	1.501 (8)
N(3)—C(8)	1.481 (7)	C(9)—C(12)	1.476 (7)
N(3)—C(9)	1.290 (7)	C(11)—C(12)	1.494 (8)
N(1)—Cu—N(2)	79.91 (18)	Cu—N(5)—C(13)	172.8 (5)
N(1)—Cu—N(3)	168.65 (17)	N(1)—C(2)—C(1)	122.5 (5)
N(1)—Cu—N(4)	92.29 (18)	N(1)—C(2)—C(3)	113.1 (5)
N(1)—Cu—N(5)	97.94 (20)	C(1)—C(2)—C(3)	124.4 (5)
N(2)—Cu—N(3)	105.86 (17)	N(2)—C(3)—C(2)	117.3 (5)
N(2)—Cu—N(4)	153.92 (16)	N(2)—C(3)—C(4)	123.3 (6)
N(2)—Cu—N(5)	103.29 (18)	C(2)—C(3)—C(4)	119.4 (6)
N(3)—Cu—N(4)	78.26 (17)	N(2)—C(5)—C(6)	112.9 (5)
N(3)—Cu—N(5)	90.31 (20)	C(5)—C(6)—C(7)	100.8 (6)
N(4)—Cu—N(5)	102.42 (18)	C(5)—C(6)—C(7′)	138.0 (12)
Cu—N(1)—O(1)	123.3 (4)	C(6)—C(7)—C(8)	107.6 (7)
Cu—N(1)—C(2)	116.7 (4)	C(6)—C(7′)—C(8)	126.1 (13)
O(1)—N(1)—C(2)	119.7 (5)	N(3)—C(8)—C(7)	115.7 (7)
Cu—N(2)—C(3)	112.0 (4)	N(3)—C(8)—C(7′)	116.2 (8)
Cu—N(2)—C(5)	130.2 (4)	N(3)—C(9)—C(10)	124.6 (5)
C(3)—N(2)—C(5)	117.8 (5)	N(3)—C(9)—C(12)	116.6 (5)
Cu—N(3)—C(8)	124.2 (4)	C(10)—C(9)—C(12)	118.9 (5)
Cu—N(3)—C(9)	113.9 (3)	N(4)—C(12)—C(9)	113.3 (5)
C(8)—N(3)—C(9)	121.1 (5)	N(4)—C(12)—C(11)	123.7 (5)
Cu—N(4)—O(2)	123.8 (3)	C(9)—C(12)—C(11)	123.1 (5)
Cu—N(4)—C(12)	117.6 (3)	S—C(13)—N(5)	179.4 (5)
O(2)—N(4)—C(12)	118.5 (4)		

Method used to solve and refine structure: direct and Fourier methods, full-matrix least-squares refinement; H atoms by difference Fourier method and theoretical calculation. Program used: *NRCVAX* (Gabe, Le Page, White & Lee, 1987).

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55755 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1017]

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{N^2-[2,2-Bis(diphenylphosphino)ethyl]-N^1,N^1-dimethylethane-1,2-diamine}-1$\kappa^2$$P$,$P'$:2$\kappa^2$$N^1$,$N^2$-tetracarbonyl-1$\kappa^4$$C$-dichloro-2$\kappa^2$$Cl$-molybdenumzinc(II), a Bimetal Complex with a Hetero-Bifunctional Ligand

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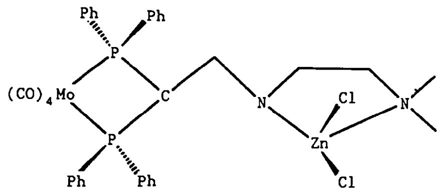
Abstract

The two metal centres of the complex are Mo with an octahedral and Zn with a tetrahedral coordination sphere. Both metal atoms are members of chelate ring systems; the Mo atom belongs to a four-membered non-planar MoP_2C ring and the Zn atom is part of a five-membered diamine chelate ring.

Comment

In recent work we prepared new hetero-bifunctional ligands and their bimetal complexes (Haupt, Kleineberg & Flörke, 1993). With N^2-[2,2-bis(diphenylphosphino)ethyl]-N^1,N^1-dimethylethane-1,2-diamine (EPP-4C2N) as ligand, the compounds [M(CO)$_4$(EPP-4C2N)M'Cl$_2$] with

M = Cr, Mo, W and M' = Zn, Cd, Hg were obtained. Here we report the crystal structure of the Mo-Zn complex (I).



(I)

The molecule has two metal centres: one four-membered diphosphane chelate ring that comprises the Mo atom in a distorted octahedral coordination, and a five-membered diamine chelate ring with the Zn atom in a distorted tetrahedral ligand-atom arrangement. The diphosphane chelate ring is one of the rare examples of reported MoP_2C-ring structures with sixfold coordination of the Mo atom. The ring is non-planar with a dihedral angle of 28.3° between the planes MoP_2 and P_2C; the greatest deviations of ring atoms from the best MoP_2C plane are −0.19 and 0.24 Å. Bond angles in the ring are P—Mo—P of 66.2 (1), P—C—P of 94.0 (1) and two Mo—P—C angles of average value 96.0 (1)°. The Mo—C bonds *trans* to the phosphine ligands tend to be shorter than those of the carbonyl groups that are *trans* to each other. These structural parameters agree well with those reported for other MoP_2C rings with octahedral Mo coordination (Cheung, Lai & Mok, 1971; Fild, Handke & Sheldrick, 1980).

The four ligand atoms of the tetrahedrally coordinated Zn atom are two terminal Cl ligands and a secondary and a tertiary amine N atom from the diamine chelate. The endocyclic N—Zn—N angle of 86.0 (1)° is drastically reduced from the ideal tetrahedral value. The opposite exocyclic Cl—Zn—Cl angle is 128.5 (1)° and reflects a strong σ-bonding contribution to the Zn—Cl bonds. In the related Cr-Zn complex [Cr(CO)$_4$(EPP-5C2N)ZnCl$_2$] with dimethylpropane (5C2N) as ligand (Haupt, Kleineberg & Flörke, 1993), the Zn atom belongs to a sixfold chelate ring with the same type of ligand atoms. In this larger and more flexible ring, the corresponding angles are 95.9 (1)° for N—Zn—N and 119.7 (1)° for Cl—Zn—Cl, respectively. The remaining Cl—Zn—N angles are in the range 96.4 (1)–117.1 (1)° for the five-membered ring and 104.5 (1)–112.3 (1)° for the six-membered ring. These changes indicate reduced ring strain of the six-membered ring. The Zn—N(secondary) bond distances are, in both compounds, longer [2.174 (2) and 2.090 (3) Å] than the Zn—N(tertiary) bonds [2.087 (2) and 2.066 (4) Å]. The average Zn—Cl bond distances are the same for both complexes [2.217 (2) and 2.215 (2) Å].

The replacement of Mo by the homologous Cr atom leads to minor changes of the MP_2C-ring parameters. The P—M—P angle enlarges by 2.3° from Mo to Cr. The P—C—P and M—P—C angles remain largely unaffected; they increase by 1.4 and 0.8°, respectively, as is true for the above-mentioned dihedral angles which differ only by about 0.5°.

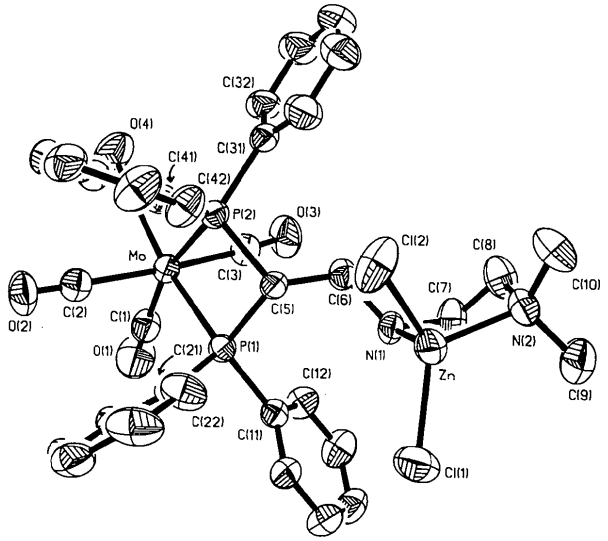


Fig. 1. Structure of the molecule.

Experimental

Crystal data

[MoZnCl$_2$(C$_{30}$H$_{34}$N$_2$P$_2$)-(CO)$_4$]
M_r = 828.8
Triclinic
$P\bar{1}$
a = 12.274 (2) Å
b = 14.358 (2) Å
c = 10.798 (2) Å
α = 92.68 (1)°
β = 96.73 (1)°
γ = 82.36 (1)°
V = 1872.1 (5) Å^3
Z = 2
D_x = 1.470 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å

Cell parameters from 25 reflections
θ = 8–17°
μ = 1.25 mm^{-1}
T = 293 K
Prism
0.68 × 0.51 × 0.20 mm
Yellow
Crystal source: reaction of equimolar amounts of ZnCl$_2$ and *as*-4C2NMo(CO)$_4$ in methanol solution at 273 K; recrystallization from methanol

Data collection

Siemens $R3m/V$ diffractometer
ω-2θ scans
Absorption correction: empirical *via* ψ scans
$T_{\min}$ = 0.856, $T_{\max}$ = 0.988
9058 measured reflections
8608 independent reflections
6516 observed reflections [$F > 4\sigma(F)$]

$R_{\rm int}$ = 0.014
$\theta_{\max}$ = 27.5°
h = 0 → 15
k = −18 → 18
l = −14 → 14
3 standard reflections monitored every 400 reflections
intensity variation: none

Refinement

Refinement on F
Final $R = 0.033$
$wR = 0.031$
$S = 1.854$
6516 reflections
367 parameters
H-atom parameters not refined, fixed at idealized positions with common $U_{\text{iso}} = 0.08$ Å^2; phenyl groups treated as rigid bodies (C—C 1.395, C—H 0.96 Å)
Calculated weights $w = 1/[\sigma^2(F)+0.0001F^2]$
$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta\rho_{\text{max}} = 0.73$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.52$ e Å^{-3}

Scattering factors, structure solution and refinement, and all calculations: *SHELXTL-Plus* (Sheldrick, 1990). Other programs: *PARST* (Nardelli, 1983); *MISSYM* (Le Page, 1987).

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mo	0.2231 (1)	0.1128 (1)	0.9243 (1)	0.035 (1)
Zn	0.4419 (1)	0.3657 (1)	0.5127 (1)	0.048 (1)
Cl1	0.5283 (1)	0.4578 (1)	0.6524 (1)	0.070 (1)
Cl2	0.2658 (1)	0.3816 (1)	0.4364 (1)	0.069 (1)
P1	0.3131 (1)	0.2535 (1)	0.8780 (1)	0.033 (1)
P2	0.1631 (1)	0.1745 (1)	0.7094 (1)	0.035 (1)
C1	0.3025 (3)	0.0845 (2)	1.0924 (3)	0.051 (2)
O1	0.3496 (2)	0.0672 (2)	1.1883 (3)	0.082 (2)
C2	0.1007 (3)	0.1947 (2)	1.0089 (3)	0.045 (2)
O2	0.0330 (2)	0.2360 (2)	1.0591 (2)	0.068 (2)
C3	0.3384 (2)	0.0195 (2)	0.8528 (3)	0.044 (2)
O3	0.3999 (2)	−0.0387 (2)	0.8145 (2)	0.068 (2)
C4	0.1344 (3)	0.0061 (2)	0.9218 (3)	0.051 (2)
O4	0.0858 (2)	−0.0570 (2)	0.9180 (3)	0.085 (2)
C5	0.2837 (2)	0.2420 (2)	0.7037 (2)	0.034 (1)
C6	0.3762 (2)	0.1859 (2)	0.6377 (3)	0.041 (2)
C7	0.5616 (3)	0.1840 (2)	0.5734 (3)	0.056 (2)
C8	0.5451 (3)	0.1860 (2)	0.4349 (3)	0.061 (2)
C9	0.6478 (3)	0.3139 (3)	0.3896 (4)	0.078 (3)
C10	0.4834 (3)	0.2866 (3)	0.2619 (3)	0.068 (3)
N1	0.4672 (2)	0.2415 (2)	0.6255 (2)	0.040 (1)
N2	0.5382 (2)	0.2852 (2)	0.3898 (2)	0.047 (2)
C11	0.4597 (1)	0.2646 (1)	0.9191 (2)	0.035 (1)
C12	0.5336	0.1822	0.9341	0.047 (2)
C13	0.6462	0.1871	0.9663	0.056 (2)
C14	0.6849	0.2744	0.9834	0.056 (2)
C15	0.6110	0.3568	0.9684	0.057 (2)
C16	0.4984	0.3519	0.9362	0.046 (2)
C21	0.2444 (2)	0.3696 (1)	0.9190 (2)	0.039 (2)
C22	0.2109	0.4413	0.8346	0.054 (2)
C23	0.1541	0.5263	0.8737	0.065 (3)
C24	0.1308	0.5395	0.9972	0.061 (2)
C25	0.1642	0.4677	1.0815	0.070 (2)
C26	0.2210	0.3828	1.0424	0.053 (2)
C31	0.1528 (2)	0.1007 (1)	0.5671 (2)	0.039 (2)
C32	0.1580	0.0038	0.5778	0.048 (2)
C33	0.1483	−0.0543	0.4709	0.064 (2)
C34	0.1335	−0.0154	0.3532	0.075 (3)
C35	0.1283	0.0816	0.3424	0.074 (3)
C36	0.1379	0.1397	0.4494	0.061 (2)
C41	0.0398 (1)	0.2613 (1)	0.6838 (2)	0.037 (2)
C42	0.0319	0.3375	0.6062	0.052 (2)
C43	−0.0672	0.3976	0.5867	0.060 (2)
C44	−0.1583	0.3816	0.6449	0.055 (2)
C45	−0.1504	0.3054	0.7225	0.050 (2)
C46	−0.0514	0.2453	0.7420	0.044 (2)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Mo—P1	2.522 (1)	Zn—N2	2.087 (2)
Mo—P2	2.515 (1)	P1—C5	1.878 (3)
Mo—C1	1.990 (3)	P2—C5	1.882 (3)
Mo—C2	2.056 (3)	C5—C6	1.530 (4)
Mo—C3	2.011 (3)	C6—N1	1.478 (3)
Mo—C4	1.992 (3)	C7—C8	1.487 (5)
Zn—Cl1	2.226 (1)	C7—N1	1.481 (4)
Zn—Cl2	2.207 (1)	C8—N2	1.516 (4)
Zn—N1	2.174 (2)		
P1—Mo—P2	66.2 (1)	Mo—P1—C5	95.9 (1)
Cl1—Zn—Cl2	128.5 (1)	Mo—P2—C5	96.0 (1)
Cl1—Zn—N1	96.4 (1)	P1—C5—P2	94.0 (1)
Cl1—Zn—N2	117.1 (1)	C8—C7—N1	109.7 (3)
Cl2—Zn—N1	105.8 (1)	C7—C8—N2	111.4 (3)
Cl2—Zn—N2	110.4 (1)	Zn—N1—C7	102.4 (2)
N1—Zn—N2	86.0 (1)	Zn—N2—C8	103.7 (2)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55850 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1029]

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2-η^3-Allyl-1,1,1-tricarbonyl-μ-(η^1:η^6-diphenylmethyl)chromiumpalladium(*Pd—Cr*) at 130 K

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Abstract

The introduction of the phenyl substituent at the benzyl C atom of the arene, π-coordinated by the Cr atom, does not cause any significant changes in the geometry of the binuclear complex which contains a direct Pd—Cr bond [average length 2.768(1) Å for the two independent molecules]. The Pd—C$_{\text{benzyl}}$, Pd—C$_{ipso}$ and C$_{\text{benzyl}}$—C$_{ipso}$ bond lengths [averages 2.138(3), 2.547(2) and

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